

Exhibit A

Vaporization of Complex Mixtures

By

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*A thesis submitted in partial fulfillment of
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The importance of the processes of condensation and vaporization in the production of natural gasoline and other products from natural gas is too evident to need much comment as almost every step in their manufacture is a condensation or vaporization process. Almost every change in pressure and temperature in the natural gasoline plant involves the partial condensation or vaporization of natural gas or gasoline.

Vapor pressure is probably the most distinctive property of natural gasolines, and methods of calculation used to compute the vapor pressure of natural gasoline from its composition should be carefully checked. Changes in composition and vapor pressure brought about by partial condensation or vaporization are extremely important not only in a study of vapor-lock but also in the determination of probable evaporation losses, and in the design of plant equipment.

The following treatment was developed by Dr. W. J. Podbielniak as part of his thesis submitted in partial fulfillment of the requirements for the Ph. D. degree in the University of Michigan.

RAOULT'S LAW

While Raoult's Law, which states that the partial vapor pressure of a liquid component in a solution of similar substances is equal to the vapor pressure of the pure substance at the same temperature multiplied by the mol. fraction of said substance in the solution, has been used to calculate the partial vapor pressures of hydrocarbons, its limits of accuracy when applied to the complex mixture, natural gasoline, have not been experimentally determined. This has been done in this investigation by checking the computed results against experimentally determined values. Raoult's Law has been shown to be sufficiently accurate for use in engineering calculations.

Although many references on the deviations from Raoult's Law in all sorts of binary mixtures are found in the literature, little information on the problem of more complex systems is available. According to Hildebrandt¹ paraffin hydrocarbons of the same series and close together in the series should show only small deviations from the laws of ideal solutions. Natural gasoline composed almost exclusively of the paraffin hydrocarbons, would be expected to approximate fairly closely an ideal solution, and as such obey Raoult's Law.

George Calingaert and Lauren B. Hitchcock² investigated the deviations from Raoult's Law in binary hydrocarbon mixtures. Vapor pressures experimentally determined as a function of composition are presented for the following pairs of hydrocarbons at 25° C. (77° F.): butane-pentane, butane-heptane, butane-benzene, butane-straw oil. The deviations of the total pressures as computed from Raoult's Law at 20 mol. per cent of the lighter component are as follows: butane-pentane, 4%; butane-heptane, 0%; pentane-heptane, 7%; butane-benzene, 64%; butane-straw oil, -2.6%.

A study of the article as a whole suggests the following conclusions:

1. The deviations from Raoult's Law are quite erratic.
2. In general, the more volatile component of a binary mixture of paraffin hydrocarbons has a *greater* actual partial vapor pressure, and the heavier component a *lesser* actual partial vapor pressure than calculated by Raoult's Law. The total vapor pres-

sure is found to agree more closely with that predicted by Raoult's Law than either partial vapor pressure.

3. The deviations for partial vapor pressures for these binary paraffin mixtures vary from 0 to plus or minus 16%; for the total vapor pressure up to about plus or minus 5 per cent.

4. No conclusions can be drawn concerning the behavior of even a ternary mixture, because the same hydrocarbon may show a considerable positive or negative deviation from Raoult's Law, depending on whether it is the lighter or heavier of the two in a binary mixture.

No other references dealing with paraffins were found. The explanation for this scantiness of data on the behavior of complex mixtures is doubtless found in the difficulty of analyzing such liquids or obtaining such liquids in the pure state, by the methods used until a few years ago.

EXPERIMENTAL VAPORIZATION OF NATURAL GASOLINE

The simplest way to partially vaporize any liquid mixture is to do so in one step by suddenly subjecting a quantity of the liquid to such pressure and temperature conditions that part of the liquid "flashes" into a vapor richer in the more volatile components and the rest of the liquid remains as a liquid residue containing a correspondingly increased proportion of the heavier components. When this process is so performed that all of the vapor is allowed to come to equilibrium with all of the residue, it is called an equilibrium "single flash."

This is not, however, the vaporization process with which we are most familiar. Ordinarily, the liquid is placed in a vessel, heat is supplied and the vapor evolved is continually removed. The vapor is always relatively richer in the more volatile components than the residue but both gradually become impoverished in these as the vaporization proceeds. When this vaporization process is so conducted that none of the vapor is refluxed and at such a rate that equilibrium practically obtains between the liquid and vapor phases, then we have another more complex type of vaporization process called "equilibrium differential vaporization." The common, although special case, is the one where the pressure is constant, usually atmospheric, although the above definition allows any pressure-temperature path, provided equilibrium is always maintained (an infinitely slow rate of vaporization required in the ideal case) and provided the vapor is removed as fast as it is formed with no accumulation of it above the residual liquid.

The apparatus described was designed for the controlled differential vaporization of a natural gasoline sample at a constant pressure of 760 mm., with provisions for taking samples of the liquid and vapor phases as often as desired and with instruments for measuring the temperature, pressure, and amount of residual liquid.

DIFFERENTIAL VAPORIZATION

Apparatus

The main part of the apparatus (Fig. 20) is the vaporizer (1) made of 16" length of 8" pipe with welded ends as shown, a bottom outlet (11) for gasoline samples, a vapor outlet (14) heated with a resistance element to prevent refluxing, and an agitator assembly (12). The agitator assembly consists of three concentric iron pipes, respectively $\frac{1}{8}$ ", $\frac{3}{8}$ ", and $\frac{3}{4}$ " pipe-size welded together as shown to allow a mercury seal in the annular spaces. The agitator is thus perfectly gas tight for pressures from about 200 mm. to about 800 mm. abs. while rotating on bearings provided by the pipe ends resting on the welds. A $\frac{1}{4}$ " steel rod shown in the center of the agitator carries a $1\frac{1}{2}$ " carpenter's augur bit (5) which rotates so as to lift liquid in the perforated pumping tube (6),

¹Solubility, American Chemical Society, Monograph, Chemical Catalogue Company, 1924.

²Journal of the American Chemical Society, Vol. 49, March, 1927, page 750.

thus effecting vigorous agitation of the contents of the vaporizer. The vaporizer is further equipped with a connection to an open arm manometer (13), with a cork float (4) surmounted by an aluminum wire pointer which slides up and down in a glass tube

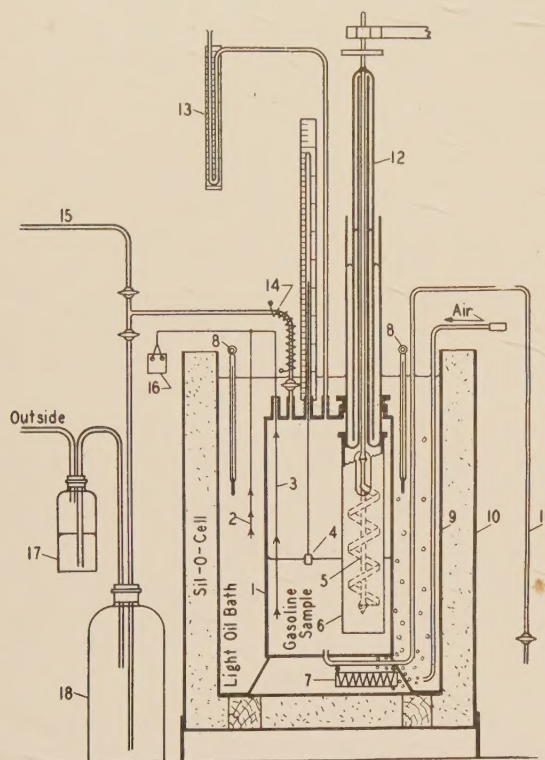


FIG. 20.—Differential vaporization apparatus

with a meter stick scale affixed, and with three triple thermocouple junctions (3) of copper constantan with the cold junctions (2) in the oil heating bath to indicate on the millivoltmeter (16) the slightest temperature difference between the heating bath and the gasoline. The light oil heating bath was heated with an electrical resistance heating element (7) which was connected in series with a variable resistance outside the apparatus to control the rate of heating. The bath was stirred vigorously with compressed air from the bottom. Thermometers (8) gave the temperature of the heating bath. The oil bath and the vaporizer assembly were placed in a double can (9) 18" x 25" and (10) 22" x 28", with Sil-O-Cell in the annular space for thermal insulation. A three-gallon bottle (18) served as a pressure equalizer and as a trap for condensed vapor. A small bottle (17) partly filled with mercury was used to maintain the desired pressure difference between the vaporizer and the atmosphere, the vapor being forced to bubble through a greater or lesser height of mercury. Practically all the connections were of $\frac{1}{8}$ " copper tubing soldered into $\frac{1}{8}$ " needle valves and secured into $\frac{1}{4}$ " pipe nipples at the vaporizer using S. A. E. gasoline connections. Connection (15) was used for sampling the vapor.

The cork float (4) was calibrated by pouring measured volumes of water into the vaporizer and reading the float height on the meter scale. The thermocouples were individually calibrated against a standard thermometer.

Procedure

The vaporizer was first completely purged of all water remaining from the volume calibration by first draining off the water through

the copper tube (11) and then maintaining the oil bath at a temperature of about 120° C. or 250° F. for about eight hours while air was blown through the vaporizer through the same line and vented through lines (14) and (15). The bath was then allowed to cool to about room temperature and a natural gasoline sample contained in a pressure cylinder was forced by its own vapor pressure into the vaporizer through the line (11). After the necessary preliminary venting in the vaporizer, the composition of the liquid was determined by fractional distillation analysis somewhat similar to the method for motor fuel analysis described in the fifth part of this report but particularly designed for analysis of natural gas and gasoline.¹

TABLE III

PERCENTAGE COMPOSITION OF ORIGINAL LIQUID

	By Liquid Volume	By Weight	In Mol. Per Cent
Propane.....	1.0	.8	1.4
Iso-butane.....	3.6	3.3	4.7
N-Butane.....	17.9	16.0	22.6
Iso-pentane.....	10.1	9.7	11.1
N-pentane.....	18.5	17.8	20.3
Iso-hexane.....	8.8	8.9	8.5
N-hexane.....	15.2	15.4	14.7
Residue.....	24.9	28.1	16.7
	100.0	100.0	100.0

In order to avoid any condensation in the connections when sampling the vapor the needle valve (14) was cracked to keep the proper pressure in the vaporizer and the vapor sample taken under reduced pressure directly into the fractionating column. In the case of liquid samples the only precaution needed was that of purging a measured amount (about 30 cc.) before sampling. The float reading was taken directly after each sample.

After taking the initial samples no further vapor was vented from the vessel except under such conditions that the total pressure in the vaporizer was 757.3 mm.² with no air present and with vigorous agitation of the gasoline sample and of the oil bath; the rate of vaporization was maintained less than 10 cc. a minute, so that the difference between the pressure in the vaporizer when vaporizing and when vaporization was stopped for a half minute did not exceed one to two millimeters of mercury; the rate of vaporization was retarded when necessary so that the difference in temperature between the gasoline and oil bath did not exceed 0.1° C. as indicated by the thermocouples. To correct for variation in the barometric pressure the glass tube through which vapor bubbled through mercury in the bottle (17) was periodically adjusted in the cork to keep the vaporizer pressure at 760 mm. as indicated by manometer (13). Connection (15) was closed when vaporizing for the purpose of reducing the volume of the gasoline; it was used only for sampling the vapor in which case the lower valve shown was closed and the upper one opened. The temperature of the oil bath was gradually raised using heater (7) and vaporization effected as explained above until it was desired to take another pair of samples. After sampling both liquid and vapor as described above, vaporization was resumed. This procedure was followed until about half of the liquid had evaporated. In all, seven liquid and seven vapor samples were taken.

¹The methods of analysis used were developed at the University of Michigan in 1925 by Walter Podbielniak and E. H. Leslie in an investigation financed by the Phillips Petroleum Company and will be described in a later paper.

²Corrected value from manometer reading of 760 m.m.

TABLE IV
DATA ON EXPERIMENTAL DIFFERENTIAL VAPORIZATION

Gasoline Temperature °C.*	Volume Residual Liquid Corrected to 0°C.	Volume Withdrawn for Liquid Samples Corrected to 0°C.	Composition of Liquid Sample in Mol %							
			Propane	Iso-Butane	Butane	Iso-Pentane	Pentane	Iso-Hexane	Hexane	Residue
21.1	10562		1.44	4.66	22.63	11.06	20.33	8.48	14.70	16.70
27.4	9215	140	.59	1.96	20.30	16.62	17.90	7.60	19.28	15.74
33.4	8140	78	.05	.98	15.90	14.13	19.47	18.39	14.67	16.41
42.0	6638	106			9.70	15.52	18.33	12.42	20.40	23.63
45.0	6182	173			8.22	8.65	22.23	9.74	26.95	24.21
50.7	5291	91			4.63	6.18	22.88	16.61	19.63	30.06
52.6	4981				4.60	4.47	22.74	23.12	16.09	28.97

Composition of Vapor Sample in Mol %						Calculated Specific Gravity at 0°C.	Mols per cc. at 0°C. of Residual Liquid	Corrected Mol Series
Propane	Iso Butane	Butane	Iso Pentane	Pentane	Residue			
13.92	10.75	43.91		21.06	4.96	.669	.008154	100
7.68	8.95	48.60	12.90	14.06	7.81	.672	.008082	87.80
2.28	8.56	46.23	16.10	16.98	9.85	.676	.008031	77.80
0.00	4.93	36.15	16.08	26.76	16.08	.687	.0076026	61.02
0.00	0.00	34.56	22.13	23.32	19.99	.690	.007496	56.03
0.00	0.00	25.78	18.58	31.18	24.46	.699	.007232	47.77
0.00	0.00	21.30	24.23	26.34	28.13	.697	.007270	46.04

*The total pressure was maintained at 757.3 mm. (corrected for temp.)

Results

All the data on the experimental differential vaporization process are summarized in Table IV. The "Corrected Mol. Series" represents the number of mols. that would have been left in the residual liquid, if no liquid had been withdrawn, and was calculated from the data in the columns headed "Volume Residual Liquid Corrected to 0° C.," "Volume Withdrawn for Liquid Samples Corrected to 0° C.," and "Mols. per cc. of Residual Liquid."

SINGLE FLASH

Apparatus

The apparatus¹ used to vaporize natural gasoline by the single flash process, Figure 21, was practically the same as the Equilibrium Flash Vaporizer described in the First Annual Report.

It consists essentially of (1) a feeding device to supply material to the heating coil at a visible and controllable rate, (2) a coil to heat and partially vaporize the liquid previous to its admission to the equilibrium chamber, (3) an equilibrium chamber in which the vapor produced is contacted with a liquid containing the same components, (4) a condenser to recover the vapor liberated in the equilibrium chamber, (5) a residuum cooler, (6) a constant-temperature bath, and (7) a liquid air trap for condensing the extremely volatile parts of the distillate.

Procedure

The material used for experiments with the single flash apparatus was a sample of commercial aviation motor fuel made by fractionating natural gasoline. This material was chosen rather than a more volatile grade of gasoline to avoid vaporization losses in the experiments. The sample was placed in the brine-cooled 1,000 cc. buret A. The heating bath H was brought to the desired temperature using the heating element U. Brine was circulated through the jackets of the vapor condenser L and the residuum cooler N. Vent E was opened to air manometer F filled with

water and stopcock C partially opened to allow the solution in the jacket to drop into the tube D and into the heating coil G, the stopcock being adjusted as often as necessary to keep the rate of feed practically constant as determined by counting the number of drops per minute. The rate used was always below 10 cc. per minute which had been proved to be adequate to bring about equilibrium between vapor and liquid in this apparatus. As soon

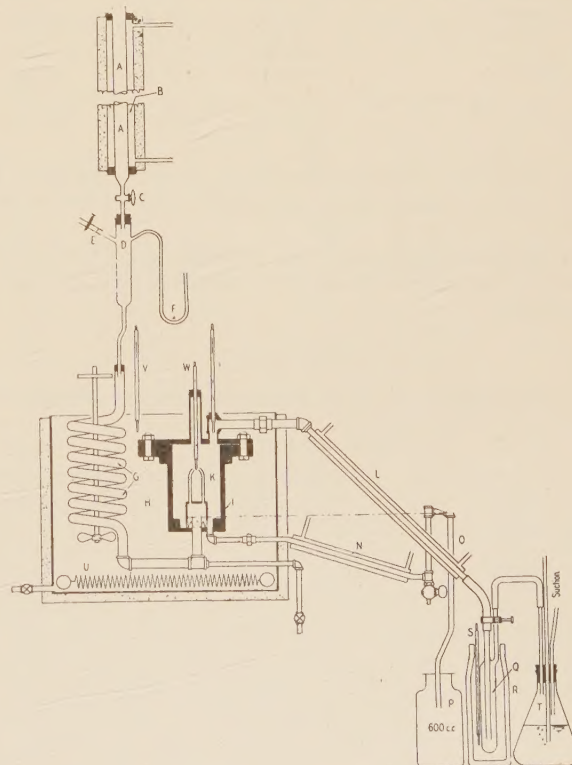


FIG. 21.—Equilibrium flash vaporizer

¹This apparatus is similar to the apparatus for the flashing of petroleum described by E. H. Leslie and A. J. Good in *Industrial and Engineering Chemistry*, 19, 453, April, 1927.

as residue began to overflow into the receiver P, the height of the indicating liquid in the manometer F, when the vapor delivery line L was open to the atmosphere, was marked and vent E closed. The vapor delivery line was connected to the glass trap Q, cooled with liquid air, and the pressure in the apparatus as read on manometer F maintained constant by adjusting the pressure regulating device T as often as necessary to compensate for the increasing head of condensate in the glass trap. No difficulty was found either in controlling the rate of feed or in maintaining the pressure in the apparatus constant.

When steady conditions of pressure, temperature, and rate, were established in the apparatus preliminary runs were made, in each of which about 200 cc. of material were flashed until the yield of distillate for a given amount of feed became constant. It was found that the sum of the distillate and the residue checked the amount of material fed within $\frac{1}{2}$ of one per cent.

Results

After a number of preliminary runs at a flash temperature of 126° F., a final check run gave the following data:

TABLE V

DATA ON EXPERIMENTAL SINGLE FLASH

	Gms.
Material fed to apparatus.....	422.0
Distillate.....	121.0
Residue.....	302.5
Distillate plus residue.....	423.5

ANALYTICAL RESULTS

	Feed Mol. %	Distillate Mol. %	Residue Mol. %
N-butane.....	5.42	11.68	2.00
Iso-pentane.....	11.85	17.86	9.54
N-pentane.....	32.10	44.56	22.77
Iso-hexane.....	13.82	12.59	11.05
N-hexane.....	16.54	8.46	24.17
Residue.....	20.27	4.84	30.48
	100.00	100.00	100.00

From the data on this run the yield of distillate was computed to be 33.93 mol. per cent of the feed and the yield of residue 66.07 per cent.

From these percentages and from the analytical data the following material balance for the individual components of the gasoline was obtained:

TABLE VI

MATERIAL BALANCE IN MOLS. FOR SINGLE-FLASH EXPERIMENT

(Basis, 100 mols. feed)

	From Analysis of Feed	From Analysis of Distillate and Residue
N-butane.....	5.42	5.28
Iso-pentane.....	11.85	12.36
N-pentane.....	32.10	30.17
Total pentanes.....	43.95	42.53
Iso-hexane.....	13.82	11.57
N-hexane.....	16.54	18.84
Total hexanes.....	30.36	30.41

It will be noted that the combined pentanes and the combined

hexanes check much closer than the individual isomers; this is due to the difficulty in separating these isomers in fractional distillation because of the small differences in boiling points. The discrepancies are not serious as the isomers have the same molecular weight and their vapor pressures are not widely different so that a considerable error in the separation of two isomers will not cause an appreciable error in the calculated vapor pressure for the combined isomers, as is shown in Table VI. On the whole the agreement is satisfactory.

CALCULATION OF VAPORIZATION PROCESSES

The differential vaporization process may be considered as a series of successive small single-flashes. The mathematical analysis of both the single flash and the differential process for any mixture is presented most simply as follows:

Let "x" be the composition of the liquid expressed in mol. fraction. Let "y" be the composition of the vapor in contact with the liquid, also in mol. fraction. Let "w" be the amount of the liquid expressed in mols.

A material balance for the components of a binary or complex mixture before and after a vaporization process, regardless whether this vaporization be an infinitesimal step in a differential vaporization process, or a finite single flash, may be expressed as the following differential equation:

$$wx = (w + dw)(x + dx) - dw(y + dy) \quad (10)$$

Since the only assumption involved in this equation is that of a material balance for each of the components of the mixture, it is of general application. It may be put into the integral form to define mathematically the *general differential vaporization process*:

$$\int_{w_2}^{w_1} \frac{dw}{w} = \int_{x_2}^{x_1} \int \frac{dx}{y-x}$$

of which the left hand side is readily integrated:

$$\log_e \frac{w_2}{w_1} = \int_{x_1}^{x_2} \frac{dx}{y-x} \quad (11)$$

When the relation between "x" and "y" is known for a differential vaporization process the right-hand side of Equation 11 may be integrated either directly or graphically for simple cases such as binary mixtures. When the mixture is complex, Equation 11 must be expressed as a number of simultaneous differential equations representing separate material balances on the components in the mixture; the direct integration of these equations is difficult (or impossible) and extremely involved. It is possible, however, to make this integration for all cases where "y" can be calculated from "x" by modifying Equation (10) to adapt it to stepwise computation: this may be done by substituting finite values for the differentials, as follows:

$$wx = (w + \Delta w)(x + \Delta x) - \Delta w(y + \Delta y)$$

and

$$\frac{wx + \Delta w(y + \Delta y)}{w + \Delta w} = x + \Delta x \quad (12)$$

If the differential vaporization process to be computed is regarded as a series of successive small single flashes, Equation (12) may be used to compute each single flash, provided Δw is given a sufficiently small value (preferably a constant small per cent of w) to make $\Delta w \Delta y$, the product of two small quantities, small enough not to affect the accuracy desired in the results. In the following computation of the experimental differential vaporization process Raoult's Law is used to calculate the composition of a vapor in equilibrium with liquid.

CALCULATION OF EXPERIMENTAL DIFFERENTIAL VAPORIZATION PROCESS

Since the experimental vaporization process was carried out at constant pressure (757.3 mm.) the pressure temperature path of the process was definitely known. The analytical data for the process were leveled by plotting them against the boiling point of the residual gasoline and drawing smooth curves through the experimental values; the following composition for the initial liquid in the vaporizer was taken from these curves:

	Mol. Per Cent
Propane.....	1.43
Iso-butane.....	4.66
N-butane.....	22.81
Iso-pentane.....	16.10
N-pentane.....	17.20
Iso-hexane.....	12.70
N-hexane.....	9.50
Residue.....	15.60
	100.00

The computation is based on this initial composition and on a constant pressure of 757.3 mm. and consists of a number of steps

each calculated exactly as shown in Table VII which gives the complete computation for the first two steps. Column 2 in the first step gives the distribution of hydrocarbons in 84.900 mols. of the initial composition. Under Column 3 are found the vapor pressures of the hydrocarbons indicated in Column 1, at the boiling point (21.1° C., about 69° F.) of the liquid in Column 2. Column 4 is obtained by multiplying Column 2 by Column 3, the products being proportional to the partial vapor pressures of the hydrocarbons in the liquid at 21.1° C. Column 5 is given to the computation of 5 per cent of the liquid (in mols.) which is the amount to be vaporized in this step, as this quantity was found small enough for the accuracy desired and large enough to expedite the work of calculation. Column 6 is obtained by multiplying Column 4 by the amount of liquid to be vaporized and dividing by the total of Column 4, this being equivalent to calculating the composition of the vapor withdrawn from the liquid by Raoult's Law. The mols. of the individual hydrocarbons in Column 6 are subtracted from the corresponding figures in Column 2 to give the residual liquid from this vaporization, in Column 7. Using the same vapor pressures as in Column 3, the partial vapor pressures of the components in this residual liquid are calculated by multiplying the figures in Column 3 by the corresponding mol. fraction in the residual liquid to give Column 8 and the column added to obtain the total vapor pressure at 21.1° C. The boiling point of this residual liquid at 757.3 mm. may be estimated from the vapor pressure chart and used to determine the vapor pressure (Column 3) of the second step. Columns 2-a and 2-b are the mol. per cent and cumulative mol. per cent compositions of the liquid in Column 2; Columns 6-a and 6-b are mol. per cents and cumulative mol. per cents of the vapor in Column 6. It was found convenient to refer the totals of all the columns 2 to 100.00 mols. These

TABLE VII

THEORETICAL COMPUTATION BASED ON RAOULT'S LAW OF THE EXPERIMENTAL DIFFERENTIAL VAPORIZATION PROCESS FOR THE SAME CONDITIONS AND FOR THE SAME ORIGINAL LIQUID COMPOSITION

FIRST STEP											
1 Compd.	2 Mols. L	3 V. P. 21.1°C.	4 (2X3)	5	6 Mols. V	7 Mols. L	8 Partial V. P.	2-a Mol. %L	2-b Cum. %L	6-a Mol. %V	6-b Cum. %V
C3	1.214	6400	7770	84.90X5% = 4.245 4.245 X (4) = (6) 66,749	.494	.720	57.1	1.43	1.43	11.64	11.64
C4-i	3.956	2370	9376		.596	3.360	98.5	4.66	6.09	14.04	25.68
C4-n	19.366	1635	31663		2.014	17.352	352.1	22.81	28.90	47.46	73.14
C5-i	13.669	597	8160		.519	13.150	97.4	16.10	45.00	12.23	85.37
C5-n	14.603	443	6469		.411	14.192	78.0	17.20	62.20	9.68	95.05
C6-i	10.782	200	2156		.137	10.645	26.4	12.70	74.90	3.23	98.28
C6-n	8.066	126	1016		.064	8.002	12.5	9.50	84.40	1.51	99.79
Res.	13.244	10.5	139		.009	13.235	1.7	15.60	100.0	.21	100.0
	84.900 (100.00%)		66,749		4.244	80.656	723.7	100.0		100.0	
SECOND STEP											
1 Compd.	2 Mols. L	3 V. P. 22.5°C.	4 (2X3)	5	6 Mols. V	7 Mols. L	8 P. V. P.	2-a Mol. %L	2-b Cum. %L	6-a Mol. %V	6-b Cum. %V
C3	.720	6655	4792	80.656X5% = 4.0328 4.0328 X (4) = (6) 61,088	.316	.404	35.1	.80	.80	7.83	7.83
C4-i	3.360	2465	8282		.547	2.813	90.3	4.17	5.06	13.56	21.39
C4-n	17.352	1710	29672		1.959	15.393	344.0	21.51	26.57	48.55	69.94
C5-i	13.150	629	8271		.546	12.604	103.7	16.30	42.87	13.53	83.47
C5-n	14.192	467	6628		.438	13.754	83.9	17.60	60.47	10.85	94.32
C6-i	10.645	212	2219		.148	10.497	29.1	13.20	73.67	3.67	97.99
C6-n	8.002	134	1072		.071	7.931	13.8	9.92	83.59	1.76	99.75
Res.	13.235	11.5	152		.010	13.225	2.0	16.41	100.00	.25	100.00
	80.656 (95.00%)		61088		4.035	76.621	701.9	100.00		100.00	

values, enclosed in parentheses, are shown as mol. percentages of the original liquid.

The stepwise calculation just described is repeated until the residual liquid in Column 2 equals 46.04 mol. per cent, as this was the mol. per cent of original liquid (corrected mol. series) remaining as residual liquid at the end of the experimental differential.

In order to test the data a number of graphs, such as Figure 22, were prepared comparing partial vapor pressures of the individual hydrocarbons obtained by,

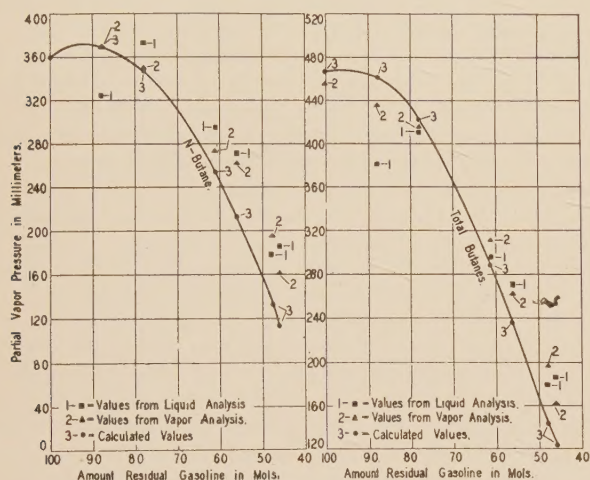


FIG. 22.—Partial vapor pressure of normal butane as determined by liquid analysis and Raoult's Law, vapor analysis, and computation from original composition by the method outlined in Table VII.

(1) Calculation from analyses of liquid samples;

(2) Calculation from analyses of vapor samples, and

(3) Calculations from the theoretical computation of the whole vaporization process from an initial composition as described above.

The deviations of the individual hydrocarbons from Raoult's Law appear less than the errors in sampling and in the analysis. The slight differences in vapor pressure of isomers which introduce error in the fractional distillation method of analysis used, tend to minimize the effect of this error in the calculations of the combined vapor pressure of the isomers. Even a large error in the apportioning of the percentage between two isomers such as iso- and normal butane involves only a small error in the calculation of the combined partial vapor pressure for both isomers, as shown in Figure 22. This error is still further minimized in the calculation of the total vapor pressure of a gasoline, which deviates scarcely one per cent from that calculated by Raoult's Law.

In order to give a better picture of the agreement of the experimental and calculated results, Figures 23 and 24 were prepared, for the liquid and for the vapor compositions respectively, the compositions being expressed in cumulative mol. per cent. These charts are best adapted for a true comparison. It is at once seen that the calculated differential vaporization process reproduces the patterns of both the liquid and vapor composition charts with satisfactory accuracy when all the difficulties in sampling, analysis, and the imperfections of the apparatus are considered.

The two charts, Figures 23 and 24, serve as a double check on the computation. The computation, however, fits both in a satisfactory manner, except for a deviation in the line dividing iso- and normal pentane, which is probably due to poor separation in the fractional distillation analyses. Although the experimental procedure is not sufficiently precise to determine the slight devia-

tions of the partial vapor pressures of the individual hydrocarbons, the above results, involving over 50 per cent vaporization, clearly indicate that Raoult's Law may be used to compute the results of a differential vaporization process within the present limits of accuracy of sampling and analysis of natural gasolines. There is a slight tendency of the lighter components in natural gasoline to vaporize more and for the heavier ones to vaporize less than required by Raoult's Law as is indicated by the fact that a vaporization step of 5 per cent used in the computation gave results closer to the experimental data than steps of 2 per cent and 4 per

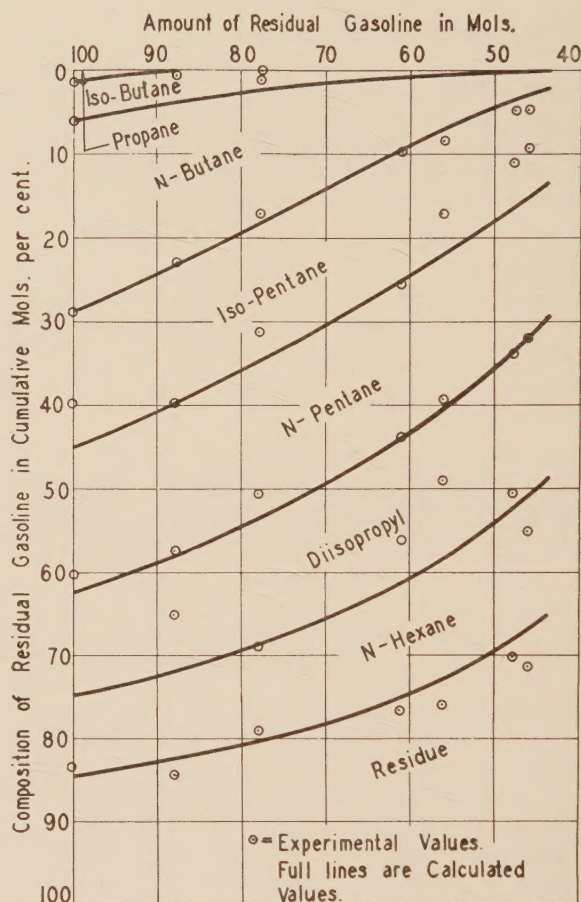


FIG. 23.—Computed and experimentally determined composition of residual liquid in the equilibrium differential vaporization process.

cent; this is in accord with the findings of Calingaert and Hitchcock¹ already discussed.

CALCULATION OF EXPERIMENTAL SINGLE FLASH PROCESS

Equation 12, which was used to calculate the small single flashes into which the differential vaporization process was divided for convenience in computation, may also be applied to the computation of a large single flash. In this case the product $\Delta w \Delta y$ may not be neglected and the single flash is calculated by setting up the proper equations for the individual components on the basis of the equality of the partial vapor pressures of the individual components in the liquid and in the vapor phase as implied in the application of Raoult's Law. The following nomenclature is used:

¹ *Journal of the American Chemical Society*, Vol. 49, March, 1927, p. 750

V = total mols. vaporized on the basis of 100 mols. of feed
V (with a subscript) = number of vaporized mols. of the component indicated by the subscript
P = total flash pressure
P (with a subscript) = vapor pressure of the component indicated by the subscript at the flash temperature

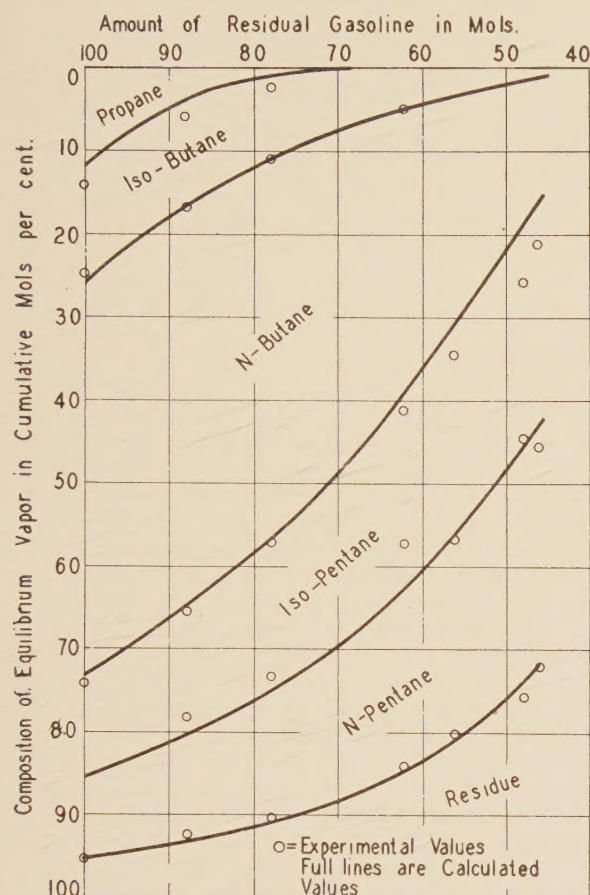


FIG. 24.—Computed and experimentally determined composition of vapor evolved in the equilibrium differential vaporization process.

In the following equations the left hand side is the product of the vapor pressure of the hydrocarbon and its mol. fraction in the liquid; the figures 5.42, 11.85, 32.10, etc., are the mol. per cents of the hydrocarbons in the feed to the single flash apparatus, as determined by analysis and reported in Table V. The right hand side is the product of the flash pressure by the mol. per cent of the hydrocarbons in the flash distillate, of which the composition is to be calculated.

$$\frac{5.42 - V_{C4-n}}{100 - V} (P_{C4-n}) = \frac{V_{C4-n}}{V} P^*$$

$$\frac{11.85 - V_{C5-i}}{100 - V} (P_{C5-i}) = \frac{V_{C5-i}}{V} P$$

$$\frac{32.10 - V_{C5-n}}{100 - V} (P_{C5-n}) = \frac{V_{C5-n}}{V} P$$

*C_{4-n} represents n-butane.
C_{5-i} represents iso-pentane, etc.

$$\frac{13.82 - V_{C6-i}}{100 - V} (P_{C6-i}) = \frac{V_{C6-i}}{V} P$$

$$\frac{16.54 - V_{C6-n}}{100 - V} (P_{C6-n}) = \frac{V_{C6-n}}{V} P$$

$$\frac{20.27 - V_{Res.}}{100 - V} (P_{Res.}) = \frac{V_{Res.}}{V} P$$

These equations may be solved for the vapor composition when any two of the variables of pressure, temperature and mol. per cent are known or assumed, using the trial method. The flash pressure in the experimental single flash was 743 mm. and the amount vaporized per 100 mols. of feed was 33.93 mols.; these values were therefore substituted in the equations and the equations reduced to a form convenient for computation:

$$V_{C4-n} = \frac{5.42}{\frac{1446.8}{P_{C4-n}} + 1}$$

$$V_{C5-i} = \frac{11.85}{\frac{1446.8}{P_{C5-i}} + 1}$$

$$V_{C5-n} = \frac{32.10}{\frac{1446.8}{P_{C5-n}} + 1}$$

$$V_{C6-i} = \frac{13.82}{\frac{1446.8}{P_{C6-i}} + 1}$$

$$V_{C6-n} = \frac{16.54}{\frac{1446.8}{P_{C6-n}} + 1}$$

$$V_{Res.} = \frac{20.27}{\frac{1446.8}{P_{Res.}} + 1}$$

For the first trial a temperature of 53.5° C. was assumed, thus fixing all the vapor pressures involved in the equations. The mols. of each component vaporized (V's) were calculated, and the sum was found to be 34.932 instead of 33.93 as it should have been, had the temperature assumed been correct. For the next trial a temperature of 52.0° C. was assumed; the sum of the mols. vapor-

ized (V) was 34.009 which is considered sufficiently close to 33.93 52.0° C. is therefore the calculated flash temperature. Since the experimental flash temperature was 52.2° C. plus or minus 0.2° C., the agreement is within the experimental error.

From the computed mols. vaporized, the composition of the distillate and the composition of the residue in mol. per cent may be obtained. Table VIII shows the agreement of the calculated with the experimental compositions of the distillate and residue.

TABLE VIII

EXPERIMENTAL AND CALCULATED RESULTS FOR SINGLE FLASH EXPERIMENT

	Vapor Mol. %		Residue Mol. %	
	Experi- mental	Calcu- lated	Experi- mental	Calcu- lated
N-butane.....	11.68	11.67	2.00	2.20
Iso-pentane.....	17.86	18.47	9.54	8.44
N-pentane.....	44.56	44.12	22.77	25.91
Total pentanes.....	62.42	62.59	32.31	34.35
Iso-hexane.....	12.59	12.30	11.05	14.61
N-hexane.....	8.46	11.22	24.17	19.27
Total hexanes.....	21.05	23.52	35.22	33.88
Residue.....	4.84	2.22	30.48	29.58

It is seen from Table VIII that the agreement of the calculated with experimental results is within about two percent for both the residue and distillate compositions when the iso and normal pentanes and hexanes are combined. When all the errors involved in conducting the single flash experiments and in the sampling and analysis are considered, it is evident that the method of computation yields results at least within the experimental error; the agreement of the calculated with the experimental results in Table VIII is as good as the material balance comparison in Table VI for amounts of components as determined by analysis of the feed and as determined by analysis of the distillate and residue. For a single flash the deviations from Raoult's Law are inappreciable and well within the experimental error, although in the differential vaporization process a trend has been noted because the deviations have there a cumulative effect.

APPLICATIONS

The methods of computation described in this paper are adequate for the solution of a variety of problems involving vaporization (or condensation) of hydrocarbon mixtures, for which substantial equilibrium between liquid and vapor may be assumed and for which the pressure-temperature conditions are known with sufficient accuracy for the purpose of the computation. The following are suggested as probable applications:

Calculation of Partial and Total Vapor Pressures.—The partial vapor pressures of the hydrocarbons in natural gasoline may be computed from its composition obtained in terms of individual hydrocarbons, with an accuracy within about 5 per cent. When the composition is known accurately through hexanes the total vapor pressure (on an air-free basis) may be calculated with an accuracy within 2 to 3 per cent. If the composition is more completely known the accuracy is correspondingly increased.

In making these calculations the molecular weight of the residue not analyzed is determined from its specific gravity and its vapor pressure assumed as that of a pure paraffin hydrocarbon, of equal specific gravity or equivalent molecular weight as given on the vapor pressure chart.

Calculation of Condensation Processes.—When a vapor of known

composition is compressed and cooled under known conditions it is possible to compute the amount and composition of the condensate and of the non-condensed gas. The design of the cooling equipment will determine what assumptions will be made as to the mechanism of the condensation process effected by it, i. e., whether approximating a simple equilibrium condensation where all of the condensate is in contact with all of the non-condensed gas or whether nearer to a true differential condensation, or perhaps best represented by three or four simple condensations.

Calculation of Distillation Processes.—The method of computing a differential vaporization process at constant pressure, as illustrated above may be applied directly to the determination of changes in composition, boiling point and vapor pressure in the distillation of gasoline when the vapor is not appreciably refluxed. When fractional distillation is to be used to effect sharper separation than possible with simple distillation it is possible to compute compositions and boiling points from plate to plate in a manner shown by previous investigators and well known to technical men.

Evaporation Losses.—Evaporation losses occur when natural gasoline is handled and exposed to air. The air layer in contact with the volatile gasoline, saturated with gasoline vapor at a partial vapor pressure equal to the vapor pressure of the gasoline is more or less rapidly removed by diffusion and fresh air brought into contact with the gasoline. While it is usually impossible to estimate the amount of contacting of gasoline with air, the composition changes for given evaporation losses may be calculated quite accurately by considering the process a differential vaporization at constant temperature. Actually the temperature may vary considerably but the composition of the vapor phase above the liquid gasoline is comparatively little affected and an average constant temperature may be assumed. The computation may also be conducted in steps each of which involves the removal of a definite and constant small volume of air-gasoline vapor, saturated with respect to the gasoline, the number of such steps taken is proportional to the amount of contacting with air and when once determined experimentally for a particular series of handling operations for a particular gasoline, may be used to calculate evaporation loss and changes in composition for other gasolines of different vapor pressure and composition handled in the same series of operations.

It is apparent from the number of possible applications that it is desirable to analyze natural gasoline through hexanes at least, as a check test on plant operation and control, and for solution of problems of equipment and plant design, as well as for research work.

CONCLUSION

Raoult's Law may be used to compute the total, and "gas-free," vapor pressure of a complex mixture of paraffin hydrocarbons such as natural gasoline with an accuracy within plus or minus 1 per cent at atmospheric temperatures and pressures.

In computing partial vapor pressures of the individual components the low boiling components exert a higher pressure and the less volatile components a lower pressure than indicated by Raoult's Law. The maximum deviation from the computed pressure in complex mixtures of paraffin hydrocarbons such as natural gasoline seldom exceeds five per cent of the partial vapor pressure.

A method has been described by which Raoult's Law may be used with satisfactory accuracy to compute changes in vapor pressure and composition of natural gases and natural gasolines, brought about by vaporization or condensation processes.

